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13. ABSTRACT (Maximum 200 words)

Shallow Si n⁺p junctions equipped with a reactively sputtered Ta₃₆Si₁₄N₅₀ amorphous metallic diffusion barrier of about 100 nm thickness have survived, without a detectable degradation of their reverse current, a 30 min long vacuum annealing test of 700 °C with Al (Al melts at 660 °C), 750 °C with Au, and 950 °C with Cu. For all three metallizations, these temperatures are records that much surpass any previously known results. This same Ta-Si-N film also acts as an excellent conducting annealing cap for GaAs. Implications of these findings are briefly discussed. A list of collaborators and of papers acknowledging the support of this contract are given.

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15 March 1989 to 14 March 1992

Development of Stable Metallization Systems

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The activities sponsored under this contract can be divided in two distinct subjects: the development of efficient thin-film diffusion barriers, and studies of contacting layers to GaAs.

The efforts on thin-film diffusion barriers have concentrated on ternary amorphous metallic alloys. The conducting oxide barriers had reached new heights of performance just at the beginning of the contract period, but the amorphous metallic alloys surpassed even these barriers by so much that we decided to focus our attention entirely on the amorphous metallic alloys. The search for truly thermodynamically stable barriers for Al was also discontinued for the same reason.

The film we studied most has the composition $Ta_{32}Si_{14}N_{50}$, obtained by reactive rf sputtering of a Ta_5Si_3 target in an argon/nitrogen mixture. Any sputtering system used to do reactive sputter-deposition of a metal can easily be converted to the deposition of Ta-Si-N simply by changing the target. This fact is important because it augurs well for the easy applicability of this type of thin-film barrier. The choice of Ta for our study was largely arbitrary. We believe that many of the early transition metals should be suitable too. We also think that Si can be replaced by other metalloids, such as B,C,P. There is probably a whole class of ternary metallic alloys with properties similar to those of Ta-Si-N. This fact forebodes well for the adaptability of these amorphous ternary metallic thin-film as diffusion barriers in applications with different requirements.

The following table summarizes the results we have obtained with the amorphous metallic Ta-Si-N thin-film barrier. The temperatures and durations given in the table are those that a shallow Si n+p junction will survive without a significant change in the reverse current of the diode upon annealing in vacuum when a diffusion barrier of Ta-Si-N about 100 nm thick separates the Si from the metal overlayer without a significant change in the reverse current of the diode. For all three metallizations, the temperatures reported here for 30 min annealing duration constitute record values that much surpass any previously reported result. The table also shows that the long-term performance at reduced temperatures is equally promising.

For comparison, the performance obtained for Ta-Si and Ta are also listed. It is clear that the addition of nitrogen to Ta-Si improves the performance in a major way.

Highest temperature, T, at which no degradation can be observed in the reverse current of a shallow n⁺p junction diode after thermal annealing in vacuum for a duration t.

Table 1

Barrier X	Test Structure	T (°C)	t
Ta ₃₆ Si ₁₄ N ₅₀	<Si>/X/Al	700	>30 min
	<Si>/X/Al	450	>1000 h
	<Si>/X/Au	750	>30 min
	<Si>/X/Au	450	>1000 h
	<Si>/X/Cu	950	>30 min
	<Si>/X/Cu	450	25 600 h
Ta ₃₆ Si ₁₄ Ta	<Si>/X/Cu	600	>30 min
	<Si>/X/Cu	450	>30 min

The major question that these results raise is why this reactively sputtered Ta-Si-N film is as outstanding a barrier as it is. The probable answer is as follows, keeping the case of Cu as the metallization in mind. (i) The composition of the film is such as to minimize its reactivity with the metal and with Si. Cu does not react with Ta and N; no stable compounds exist in these two binary systems. The only element in the diffusion barrier with which Cu can form compounds is Si and this element is present only as a minor constituent. Silicon does form a nitride and Ta silicides, but with pure N the reaction requires temperatures beyond 1000° C. It is therefore quite likely that the film is in fact thermodynamically stable with both Cu and Si (making abstraction of its metastable structural form), or that it is only weakly unstable in regards reactions with its two adjoining elements. The film thus fulfills the principal condition of chemical stability a barrier layer must meet to be stable upon thermal annealing. (ii) To act as a diffusion barrier, a film must also have low diffusivities for the adjoining elements. We surmise that this condition is fulfilled by virtue the amorphous structure of the film that precludes the presence of fast diffusion paths like grain boundaries.

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To prove or refute these ideas is the next major problem on the conceptual side of the subject. On the applications-oriented side, the next task is to develop a data base on the performance of other amorphous metallic alloys of this class of thin films.

We have also tested the Ta-Si-N films as a cap to prevent the dissociation of GaAs during thermal annealing. In those experiments, a GaAs wafer is first capped by a Ta-Si-N film. A collector is then placed on top of the capped GaAs to capture the As that may be escaping during annealing. The collector (a thin film of Cr) is then analyzed by backscattering spectrometry to quantify the loss, if any. We found that our reactively sputtered Ta-Si-N film is as effective as a conventional Si_3N_4 capping layer used industrially. The latter is insulating, while Ta-Si-N is conducting. Amorphous metallic alloys thus offer a novel solution to device processing where the capping layer required for thermal annealing can subsequently become an integral part of the device.

The ability to effectively cap GaAs during thermal processing is of major significance for the design of stable contacts to GaAs in that it permits the use of phase diagrams to predict the final outcome of metal/GaAs reactions. Without effective diffusion barriers to prevent As from escaping, the final state is unknown. Essentially all GaAs metallization studies that have been carried out to this date have been performed without a cap, that is in a thermodynamically open system. We are now in a position to approach this subject from a new and logical starting point, based on the use of phase diagrams and caps to design stable metallization systems.

Contacts with industrial and government laboratories during the period of this contract have been frequent and productive. Active interactions with the following institutions have taken place during the course of this contract: Jet Propulsion Laboratory, Rockwell International, McDonnell-Douglas, Norton Corporation, Varian Associates, Intel Corporation, and Motorola Inc., as well as with laboratories abroad (Brazil, Finland, Germany, and France).

The following individuals have participated in the activities of this contract under full or partial support or as collaborators:

Bartur, M.	Visiting Associate at Caltech, Consultant
Chen, J.S.	Graduate Student, Caltech
Dobeli, M.	Collaborator, Research Fellow, Caltech
Dorner, W.	Collaborator, Graduate Student, U. of Munster, Germany
Easterbrook, M.P.	Accelerator Engineer, Caltech
Garden, C.L.	Undergraduate Student, Caltech
Garland, C.M.	Collaborator, TEM Technician, Caltech
Gorris, R.	Laboratory Technician, Caltech
Halperin, L.E.	Graduate Student, Caltech
Kolawa, E.	Senior Research Fellow, Caltech
Lee, R.C.	Collaborator, Graduate Student, University of Wisconsin-Milwaukee
Mehrer, H.	Collaborator, Professor, U. of Munster, Germany
Raud, S.	Research Fellow, Caltech
Ruiz, R.P.	Collaborator, Jet Propulsion Laboratory
Sherman, A.	Collaborator, Varian Associates, Palo Alto, CA.
Stevens, B.	Accelerator Engineer, Caltech
Molarius, J.	Research Fellow, Caltech
Morishita, K.	Research Fellow, Caltech
Nicolet, M-A.	Professor, Caltech
Nieh, C.W.	Collaborator, Research Fellow, Caltech
Pokela, P.J.	Visiting Associate at Caltech, Lohja, Finland
Tandon, J.L.	Visiting Associate at Caltech, McDonnell-Douglas
Tombrello, T.	Collaborator, Professor, Caltech
Vu, Q.T.	Research Fellow, Caltech

One Ph.D. Thesis was completed during the course of this contract:

Pekka J. Pokela, June 14, 1991:

"Amorphous Diffusion Barriers for Electronic Applications".

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